Molecular Catalysis 440 (2017) 19–24

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

Effects of H_2O on the thermal and photocatalytic reactions of ethane on supported Au

Anita Tóth, Tamás Bánsági, Frigyes Solymosi *

MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, H-6720, Szeged, Hungary

ARTICLE INFO

Article history:
Received 30 May 2017
Received in revised form 4 July 2017
Accepted 9 July 2017

Keywords:
Photo-induced decomposition of ethane
Effects of H_2O
Production of H_2 and C_2H_4
TiO_2-supported Pt metals

ABSTRACT

The effect of illumination on the $H_2O + C_2H_6$ reaction was investigated on Au deposited on TiO_2, ZnO and CeO_2 samples. Whereas the photocatalytic decomposition of ethane is very limited even on the most active pure TiO_2: the conversion was only ~4% at 300 K in 210 min, the deposition of Au metal onto TiO_2 markedly enhanced the rate of photo-induced decomposition of C_2H_6. Addition of H_2O to ethane further enhanced the conversion and led to the production of H_2. The highest conversion of ethane, 23.5% was measured for Au/TiO_2. Ethylene was not detected even in traces, indicating the complete degradation of C_2H_6 to H_2 and carbon containing deposit. Temperature programmed reaction (TPR) measurements revealed that the carbonaceous deposit on the catalysts is very stable. On Au/TiO_2 it reacted with H_2 to give CH_4 at Tp = 453 and 604 K and C_2H_6 and C_3H_8 with Tp = 602 K. The promoting effect of metals was explained by a better separation of charge carriers induced by illumination and by the enhanced electronic interaction between metals and TiO_2.

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1. Introduction

A great attempt is being made to obtain hydrogen in economical ways. Besides the water-gas shift process, the catalytic decomposition of C—H compounds is the most suitable source of H_2 production [1–8]. Although dispersed metals are effective catalysts for the decomposition of methane and ethane, their reactions need high temperature, and we can count with the deposition of carbon leading to the deactivation of the catalysts. As in other cases the reaction can be accelerated by illumination [8–19]. The rate of the photocatalytic reaction can be further increased by using another reaction partner, CO_2 or H_2O, which may react with the hydrocarbons and/or with the carbon deposition, thereby enhancing the production of H_2 [20].

There is a growing interest in establishing how the defect structure and electric properties of oxidic supports influence the catalytic performance of deposited metals [21,22]. This interest can be led back to the early findings, namely that changing the electric conductivity of n-type TiO_2 markedly influences the catalytic efficiency of metals deposited on its surface [23–27]. The electric structure of the support was found to be decisive in the different types of reactions, such as photocatalytic decomposition of dimethyl ether [16], in the reaction of ethane with CO_2 [7], in the hydrogenation of CO_2 [20], and in the production of H_2 in the photocatalytic reactions of ethane [15].

In the present work an account is given on the H_2O-promoted thermal and photocatalytic decomposition of ethane at 300 K. The catalyst chosen is supported Au, which was deposited on various semiconduction oxides, such as TiO_2, ZnO and CeO_2.

2. Experimental

2.1. Methods

Catalytic measurements were carried out in a fixed bed continuous flow reactor made of a quartz tube. The flow rate of reactant gases was 12 ml/min. The exit gas was analysed by gas chromatograph (Hewlett-Packard 5890) on a Porapak QS column. The carrier gas was Ar which contained 12.5% of C_2H_6. In the study of $H_2O + C_2H_6$ reaction we applied a gas mixture of 1:1 mol ratio.

The photocatalytic reaction was followed in the same way as described in our previous paper [7]. The reactor was equipped with a 500 W medium pressure mercury vapor lamp (TQ 718, Heraeus Noble light, Germany) as a light source. The approximate light intensity at the catalyst films is 59.4 mW/cm^2. The photoreactor (volume: 670 ml) consists of two concentric quartz glass tubes fitted one into the other and a centrally positioned lamp. It is connected to a gas-mixing unit serving for the adjustment of

* Corresponding author.
E-mail address: fsolym@chem.u-szeged.hu (F. Solymosi).

http://dx.doi.org/10.1016/j.mcat.2017.07.008
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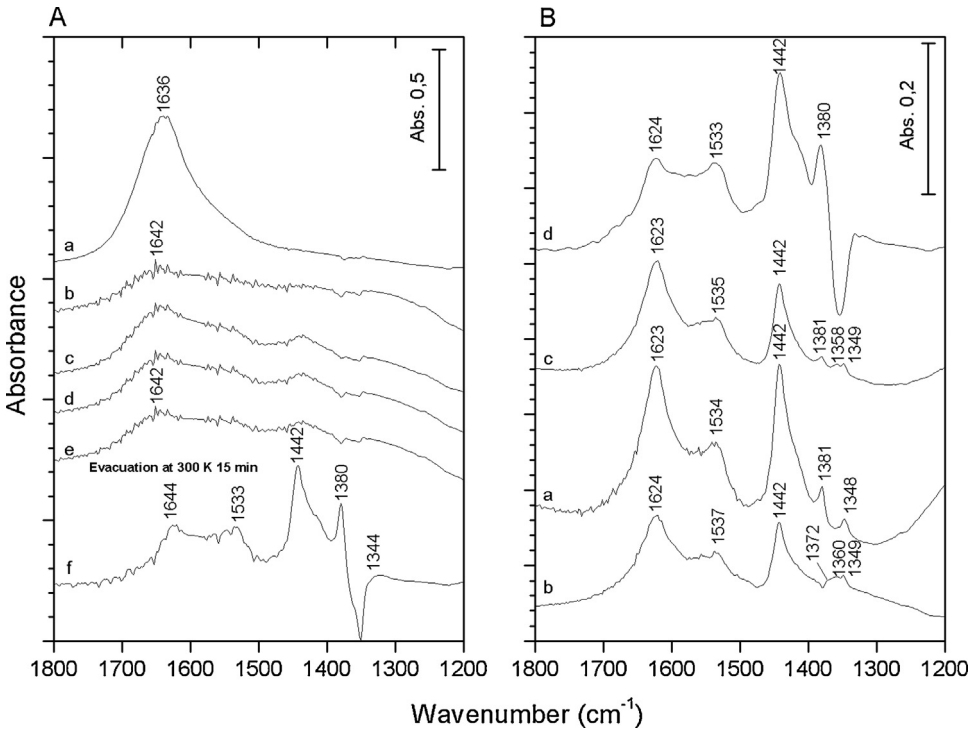

Fig. 1. (A) Effect of illumination on the infrared spectra of C_2H_6 on Au/TiO_2. (a) 0 min; (b) 5 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min after degassing. (B) Interruption of experiment and degassing the sample (a) after 15 (min): (b) 30 min; (c) 60 min; (d) 120 min.

the composition of the gas or vapor mixtures to be photolyzed in situ. The carrier gas was Ar which was mixed with C_2H_6 (~1.5%, 330 μmol). In the study of the effects of H_2O, its amount was varied between ~1.5-4.5%. The gas-mixture was circulated by a diaphragm pump. The reaction products were analysed with an Agilent 4890 gas chromatograph equipped with PORAPAK 1/2Q + PORAPAK 1/2S packed and Equity-1 capillary columns. The volume of the sampling loop of the GC was 500 μl. The amount of all products was related to this loop. The conversion of C_2H_6 was calculated taking into account the amount of C_2H_6 consumed. This value agreed well with that based on the H basis, e.g. taking into account the H content of the C_2H_6 and the amount of H_2 formed.

For FTIR studies a mobile IR cell housed in a metal chamber was used [15]. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument. Samples were illuminated by the full arc of a Hg lamp (100 W LPS-220, PTI) outside the IR sample compartment. The filtered light passed through a high-purity CaF_2 window into the cell. All the spectra presented in this study are difference spectra.

In the temperature programmed desorption (TPD) studies the heating rate was 5 K/ml and the flow rate of Ar was 20 ml/min.

2.2. Materials

1% Au/TiO_2 and 1% Au/ZnO catalysts were purchased from STREM Chem. Inc. Average gold crystallite size is ~2–3 nm. Other supported Au catalysts were prepared by a deposition-precipitation method. $HAuCl_4 \times aq$ (p.a., 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the aqueous $HAuCl_4$ solution had been adjusted to 7.5 by the addition of 1 M NaOH solution, a suspension was prepared with the finely powdered oxidic support, and the system was kept at 343 K for 1 h under continuous stirring. The suspension was then aged for 24 h at room temperature, washed repeatedly with distilled water, dried at 353 K and calcined in air at 573 K for 4 h. The other oxides used as supports were: CeO_2 (Alfa Aesar) and MgO (Reanal). The average gold crystallite size in these samples is 5–8 nm. The surface area of the catalysts was determined by BET method with N_2 adsorption at ~100 K. The dispersion of metals was determined by the adsorption of H_2 at room temperature.

3. Results and discussion

3.1. IR spectroscopic studies

In a previous paper we demonstrated that deposition of Pt metals onto TiO_2 only slightly influenced the absorption spectra of C_2H_6 at the room temperature [15]. In the case of Au/TiO_2 the adsorption of $H_2O + C_2H_6$ produced absorption bands at 3001, 2963, 2952, 2928, 2890, 2870 and 1636 cm^{-1}, which agreed well with those obtained for pure TiO_2 [15]. Illumination only slightly affected the positions of the above absorption bands. After flushing the $C_2H_6 + H_2O$ mixture absorption bands at 2972, 2935 and 2868 cm^{-1} remained in the high frequency region. New spectral features were detected at 1662, 1533, 1442, 1380 and 1344 cm^{-1} in the low frequency range, which we attribute to the different vibrations of adsorbed C_2H_4 and C_2H_x fragments formed in the photocatalytic reaction (Fig. 1A). As these absorption bands were seen only after evacuating the gas phase, in order to see the development of these bands the cell was evacuated at various times. Spectra obtained are shown in Fig. 1B. Accordingly, the above bands developed at very early stage of the photoreaction and they became somewhat larger with the increase of illumination time.

3.2. TPD measurements

Following the adsorption of C_2H_6 on Au/TiO_2 a very small amount of C_2H_4 desorbed first with Tp ~ 363 K, followed by C_2H_6 (Tp = 753 K) and CH_4 (Tp = 723 K). A larger amount of H_2 was released above 600 K with a peak of 663 and 993 K (Fig. 2). Adsorbing $H_2O + C_2H_6$ gas mixture over Au/TiO_2 gave CH_4 (Tp = 753 and 903 K) and a smaller amount of C_2H_4 (Tp = 753 K). H_2 desorbed with

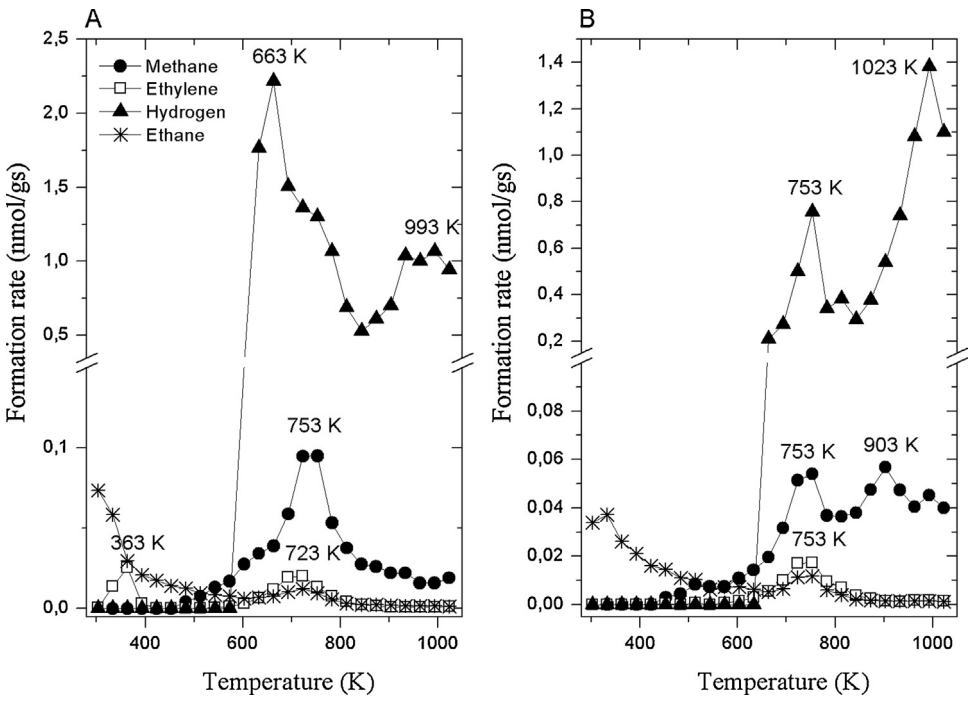

Fig. 2. Temperature programmed desorption of C_2H_6 following its adsorption over Au/TiO_2 (a) in the absence of H_2O; (b) in the presence of H_2O.

T_p = 753 and 1023 K. A very small amount of C_2H_6 continuously released above 300 K up to ~850 K.

The fact that the amount of H_2 desorbed is incomparably larger than that of C_2H_4 suggests the occurrence of the following reactions

$$C_2H_6 = C_2H_4 + H_2 \quad (1)$$

$$C_2H_4 = CH_4 + C \quad (2)$$

$$C_2H_4 = 2C + 2H_2 \quad (3)$$

The decomposition of C_2H_6 starts around 550 K. The desorption of weakly bonded C_2H_6 and C_2H_4 occurs slightly above 300 K. The main feature of TPD curves remain the same when H_2O was added to C_2H_6. Qualitatively similar TPD curves were obtained for Au/ZnO.

3.3. Thermal catalytic reaction

Fig. 3 shows the results obtained for the thermal decomposition of ethane as a function of temperature on various Au catalysts. Au/ZnO proved to be the most active: the conversion of ethane reached 10% at 773 K, whereas on other samples this value required higher temperatures to be reached. The product distribution depends on the nature of the supports. On Au/TiO_2 the same amount of H_2 and C_2H_4 was formed in the whole temperature range, on another Au sample the H_2/C_2H_4 ratio was larger than 1, and a well measurable amount of CH_4 was also produced. Adding H_2O to C_2H_6 ($H_2O/C_2H_6 \sim 1$) markedly increased the conversion of C_2H_6 on all samples (Fig. 4). Its effect was more explicit in the formation of H_2. On Au/TiO_2 the amount of H_2 increased by a factor of 5 at 950 K. Interestingly, much less enhancement occurred in the production of C_2H_4.

3.4. Photocatalytic reactions

The photo activity of previously studied Au samples was investigated at 300 K. In the absence of H_2O the illumination over supported metals led only to a very little, less than 1% decomposition of ethane. Adding H_2O to the C_2H_6 ($H_2O/C_2H_6 \sim 1{:}1$) induced only a slight photoreaction either on Au/ZnO, Au/MgO or on Au/CeO_2. The situation was completely different over Au/TiO_2. A significant amount of H_2 evolved and also a smaller amount of CO_2. This is shown in Fig. 5A. The slight formation of methane also occurred. On the basis of H_2 formed the conversion of ethane approached 25% in 200 min. The consumption of ethane gave somewhat lower values. For comparison we mention that illumination exerted only very slight effect on the decomposition of H_2O and C_2H_6 alone. In the case of H_2O we registered only 1–2% decomposition in 200 min, whereas a larger photoeffect was found for C_2H_6: in 200 min the conversion reached ~5%.

In the explanation of the high photoactivity of Au/TiO_2 we have to take into account that TiO_2 is a semiconducting oxide. The fact that on pure TiO_2 the illumination caused only a slight increase in the conversion is probably due to the recombination of the charges induced by illumination

$$TiO_2 + h\nu = h^+ + e^- \quad (4)$$

$$h^+ + e^- = h\nu \quad (5)$$

is very fast on TiO_2. The deposition of Au metal onto TiO_2, however, markedly enhanced the extent of photo-effect of TiO_2. This promoting effect of metals in photocatalytic processes is generally explained by the better separation of the charge carriers generated in the primary process [8,9], which provides a greater possibility for the activation of C_2H_6

$$C_2H_6 + e^- = C_2H_6^{\delta-} \quad (6)$$

$$C_2H_6^{\delta-} = C_2H_{5(a)} + H_{(a)} + e^- \quad (7)$$

It can be also assumed that the Schottky barrier at Au/TiO_2 interface can function as an efficient barrier preventing electron-hole recombination [10,14]. In the case of Au catalyst Wu et al. [28] pointed out that smaller metal particles induce more negative Fermi level shift than the larger particles. In addition the surface plasmon resonance absorption may also contribute to the total absorption thereby to the enhanced photoactivity of Au/TiO_2 catalyst [17,23]. As the work function of Au metal is higher (5.16 eV) than that of TiO_2 (4.6 eV), we can expect the transfer of electrons from TiO_2 to metal at the Au/TiO_2 interface contributes also to the

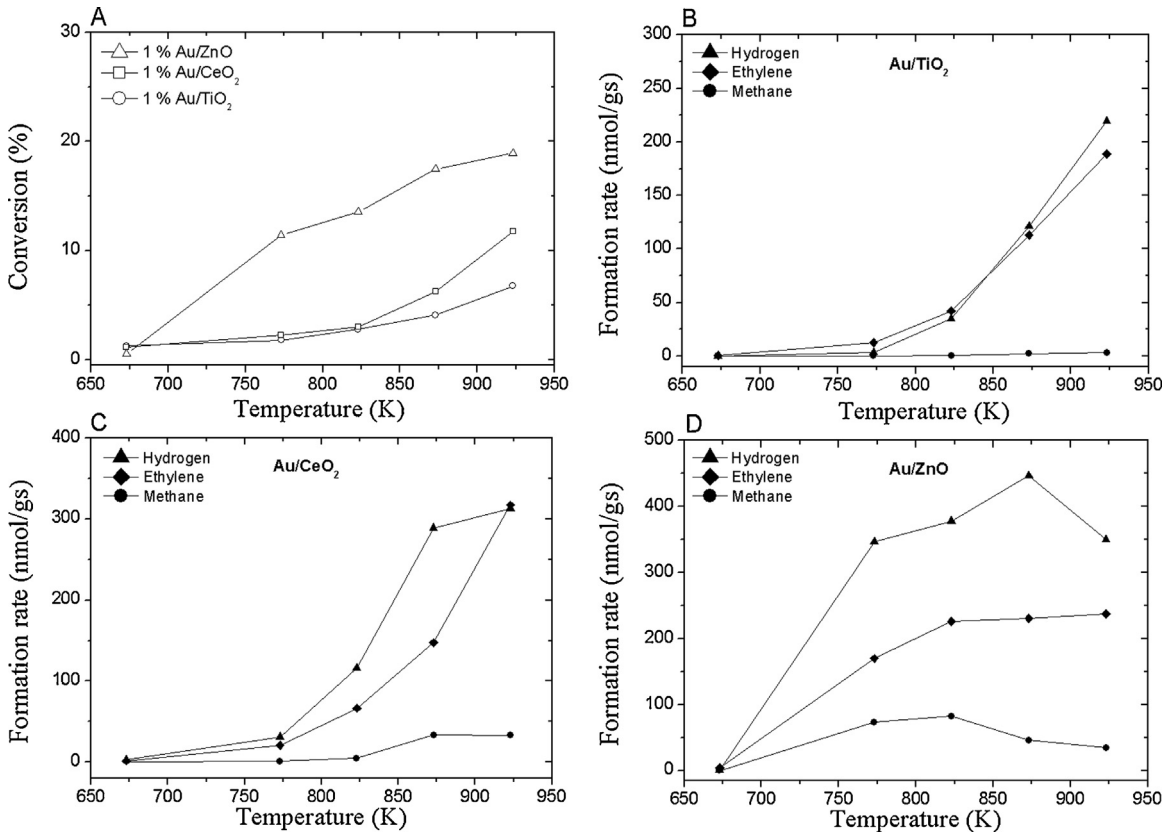

Fig. 3. Effect of support on the thermal decomposition of C_2H_6 from Au/ZnO Au/CeO_2, and Au/TiO_2.

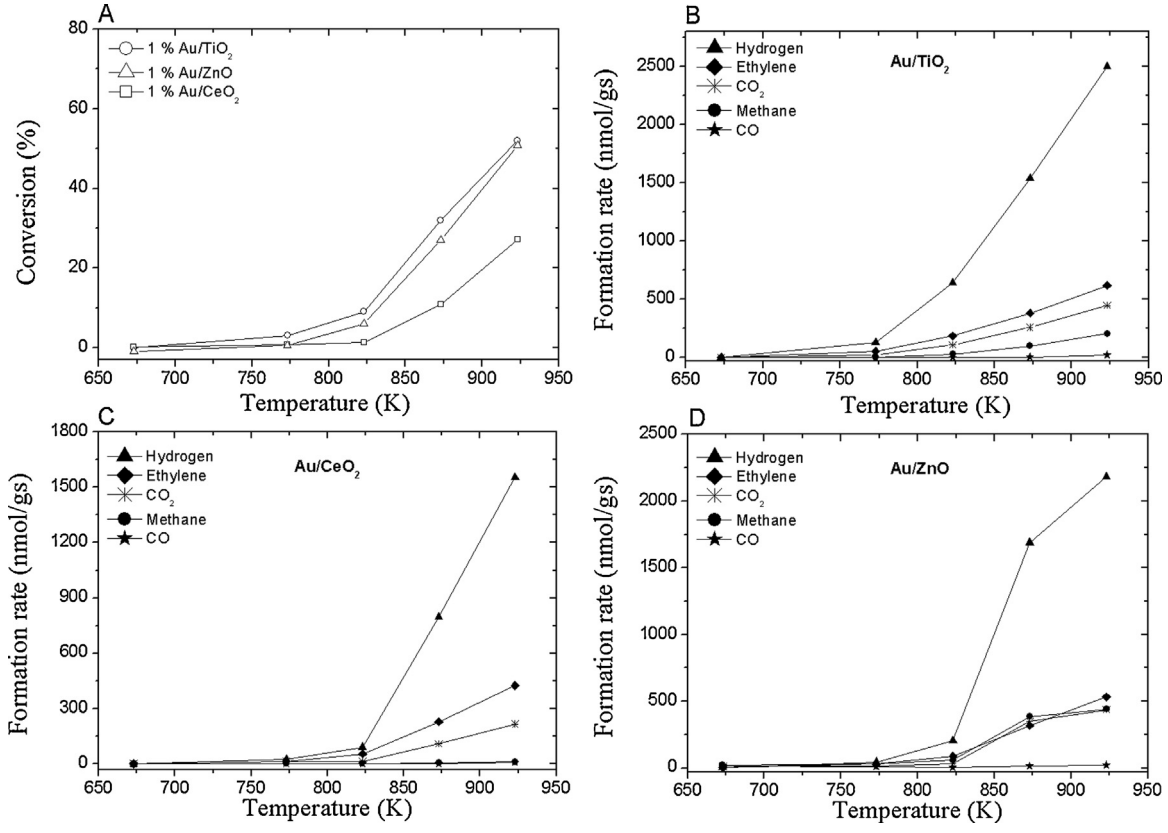

Fig. 4. Effect of H_2O on the decomposition of C_2H_6 catalyzed by supported Au catalysts.

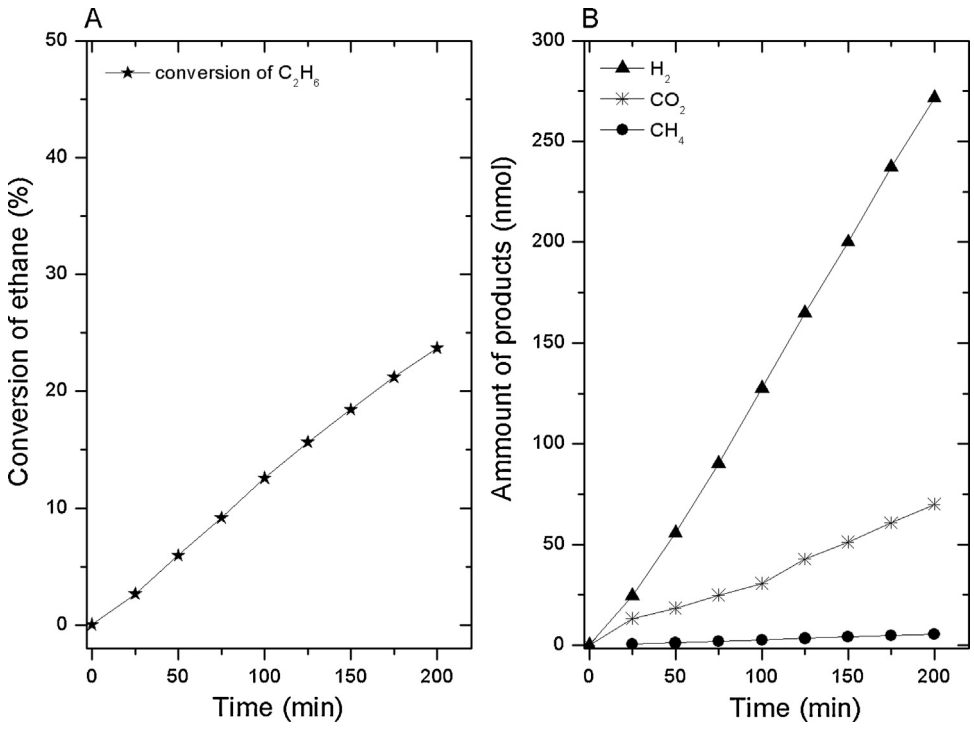

Fig. 5. Photocatalytic reaction of C_2H_6 in the presence of H_2O on Au/TiO_2 catalyst.

enhanced activation of adsorbed molecules. The role of the electron transfer in the enhanced catalytic effect of TiO_2 supported metals catalysts has been assumed and confirmed long time ago [24–27] and this idea has been generally used since then.

As regards the further steps we could assume the decomposition of C_2H_5 radical to C_2H_4

$$C_2H_{5(a)} = C_2H_{4(g)} + H_{(a)} \quad (8)$$

or as was found on many metal surfaces [29,30], its recombination

$$2C_2H_{5(a)} = C_4H_{10(a)} \quad (9)$$

The fact that neither C_2H_4 nor C_4H_{10} was detectable in the products suggests that the lifetime of transiently formed C_2H_5 or C_xH_y is very short, and instead of their coupling reactions they underwent fast photo-generated degradation resulting in some kind of carbonaceous deposit onto the catalyst.

$$C_2H_{5(a)} = C_{(s)} + 2.5\,H_2 \quad (10)$$

It is an open question how the H_2O participates in the photocatalytic process. A separate study on the photolysis of H_2O on the same Au/TiO_2 catalyst indicated that illumination induces only a very slight decomposition of H_2O, less than 2%. The possible reason is that the product of dissociation of H_2O, very likely O atoms formed in the recombination of OH groups

$$2OH_a = H_2O + O \quad (11)$$

remain the surface occupying the active center. We assume that in the case of TiO_2-containing sample the oxygen vacancies are the active centers for this process. The fact that ZnO does not contain O vacancy, but Zn excess occupies interstitial position in the lattice may be one of the reasons of the less activity of Au/ZnO compared to Au/TiO_2.

5. Conclusions

(i) n-type oxides (TiO_2, ZnO, CeO_2) only slightly catalyses the thermal and the photoreaction of $H_2O + C_2H_6$.
(ii) Deposition of Au on the above oxides enhances the thermal reaction of $H_2O + C_2H_6$ at very high temperature; the conversion exceeds 40% on the most active catalyst at 900 K
(iii) Illumination, however, induces the $H_2O + C_2H_6$ reaction over Au/TiO_2 even at room temperature resulting in 20% conversion of C_2H_6 in 200 min yielding H_2 and some CH_x fragments.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences.

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